A Non-constrained Axial t-Butyl Group in a Six-membered Ring

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Summary 5-t-Butyldihydro-1,3,5-dithiazine exists with the t-butyl substituent preferentially in the axial position with ΔG^0_{25} 0·8 ± 0·1 kcal mol^{-1}.

ELIEL[1] AND ROBINSON[2] and their co-workers have shown that in suitably substituted 5-t-butyl-1,3-dioxans, the t-butyl group exists preferentially in the axial position; however, in the examples quoted a *cis*-substituent in the 2-position, which experiences severe steric interactions when axial, provided a considerable driving force. Results from this laboratory[3] indicate that in 1,3,5-tri-t-butylhexahydro-1,3,5-triazine, one t-butyl group is preferentially axial; however, here inversions at the nitrogen atoms render each individual t-butyl group preferentially equatorial on time average. We now report an example of an unconstrained axial t-butyl group.

The dipole moments† observed for 5-methyl-, 5-ethyl-, and 5-isopropyl-dihydro-1,3,5-dithiazine‡ (1·47 ± 0·01, 1·46

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† All dipole moments values quoted refer to cyclohexane solution.

‡ The preparation of these compounds will be described in the full paper: satisfactory analytical data were obtained for all new compounds.

± 0·01, and 1·41 ± 0·01 D respectively) are all close to the arithmetic difference between the moments of 1,3-dithian (2·14 ± 0·01 D) and the corresponding 1-alkylpiperidine.[4] Models of the chair forms of the dithiazines indicate that in the conformer with the alkyl group axial the moments of the dithian and alkylpiperidine portions of the molecule are close to being antiparallel suggesting that they exist largely in this conformation rather than in the equatorial-alkyl form for which a much larger moment is expected. This conclusion is confirmed by calculations based on a total dihydrodithiazine ring moment made up of three components due to the heteroatoms and their associated C–X bonds. These calculations indicate some distortion of the axial *N*-alkyl group away from the sulphur atoms, similar to that we have postulated occurs in axial piperidines.[4]

The dipole moment of 5-t-butyldihydro-1,3,5-dithiazine‡ (1·85 ± 0·01 D), when compared with calculated moments of 1·59 and 2·75 D for the t-butyl group axial and equatorial, respectively, then indicates that this compound exists with the t-butyl group preferentially in the axial position, with ΔG^0_{25} 0·8 ± 0·1 kcal mol^{-1}.

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